

# Energy-Transfer Type Light-emitting Polymer Based on Poly(p-phenylene vinylene) and Preparation thereof

## Technical Field

This invention belongs to the field of organic optoelectronic material and technique. Particularly, it relates to energy-transfer type light-emitting polymer based on poly(p-phenylene vinylene) and preparation thereof.

## Background Art

In the field of polymeric electroluminescence, the development of highly efficient light-emitting polymers is the everlasting subject in the scientific research of material, and the effective way for improving the fluorescence quantum efficiency of light-emitting polymer is an unremitting goal of the international material scientists.

Since the electroluminescence of the conjugated polymer—poly(p-phenylene vinylene)(PPV) was reported in 1990 by Burroughs et al, Cambridge Univ., UK, the typical polymeric luminescent material systems, such as poly(p-phenylene) (PPP), polyalkylfluorene (PAF), poly alkylthiophene (PAT) have been developed in succession, the research and practicalizing courses of polymeric luminescent material have been

promoted greatly.

The ways for improving fluorescence quantum efficiency of polymeric luminescent material mainly include, for example, warping the molecules to reduce their aggregation, wrapping the molecules to weaken their aggregation, and transferring the inner molecular energy to strengthen the luminescence. For example, a high efficiency green PPV polymeric luminescent material (luminous efficiency up to 10 cd/A) has been prepared by the method of warping molecules by H. Spreitzer et al (Adv. Mater., 10, 1340, 1998; PCT Patent Application, WO 98/27136, 1996); a blue molecule-isolated type polymeric luminescent material has been designed and synthesized, by using a side group of large size dendrimer as isolated group, by Schlueter et al (Angew. Chem. Int. Ed., 38, 2370, 1999; Macromolecules, 33, 2688, 2000); and a molecule-wrapping type polymeric luminescent material has been prepared by using large size cyclic compound as insulated molecular conductor, H. L. Anderson et al, Nature Materials, 1, 160, 2002. All these methods provide a new way for developing high efficiency polymeric luminescent material.

The intermolecular energy-transfer is an universal phenomenon of the polymeric electroluminescence, and generally results in quenching of SW (short-wave) luminescence, and intensifying of LW (long-wave) luminescence, i.e. results in transferring energy from SW luminescence to

LW luminescence. Therefore, as an effective way for raising the fluorescence quantum efficiency of electroluminescent devices, it is widely used in preparing the blending type polymeric electroluminescent devices. Based on the fact that energy can be transferred between different emission components at a certain condition, we have developed one energy-transfer light-emitting polymers in which energy is transferred from main chain to side chain (Chinese Patent Application No.02116046.5) and one in which energy is transferred from side chain to main chain (Chinese Patent Application No.02118729.0) by co-polymerizing two different luminous elements onto the main chain and side chain of the polymer molecule, respectively. The above two applications were useful for developing high efficiency polymeric luminescent material. However, there is still a need for further improving the luminescent efficiency.

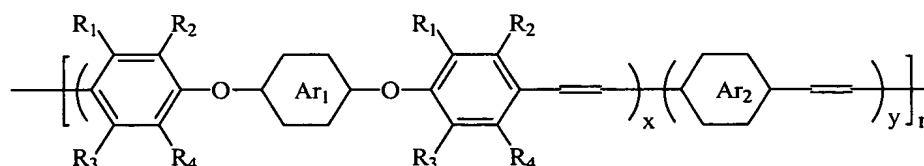
#### Summary of this Invention

An object of this invention is to provide an energy-transfer type light-emitting polymer based on poly(p-phenylene vinylene)s with the improved luminescent efficiency;

Another object of this invention is to provide a process for preparing the energy-transfer type light-emitting polymer based on poly(p-phenylene vinylene)s.

In order to achieve the above objects, the present inventors studied diligently and thoroughly. As a result, it was found that the fluorescence quantum efficiency of a polymeric luminescent material can be greatly improved. That is, different luminous elements which are fully isolated by an ether bond are contained in a backbone of a poly(p-phenylene vinylene) polymer, thus making it possible that energy transfer happens between the different luminous elements in the backbone.

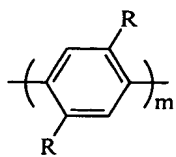
Thus, according to one aspect of the present invention, an energy-transfer type poly(p-phenylene vinylene) polymeric luminescent material is provided, which has the structural unit as represented by the following formula (1):



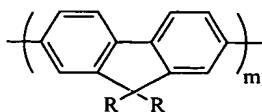
Formula (1)

wherein  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  each independently is hydrogen, alkyl, alkoxy, optionally substituted phenyl or naphthyl;  $x$  and  $y$  each is the content of the luminous element, satisfying  $0 < x \leq 1$ ,  $0 \leq y < 1$ ,  $x + y = 1$ ; and  $n = 1-200$ ;

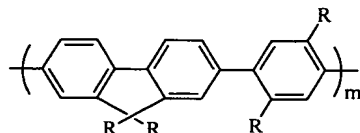
$Ar_1$  being one or two structural luminous elements selected from a group consisting of formula (2) – formula (29), wherein  $R$ ,  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  each independently is hydrogen, alkyl, alkoxy, optionally substituted phenyl or naphthyl;  $m = 1-10$ ;



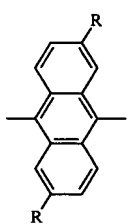
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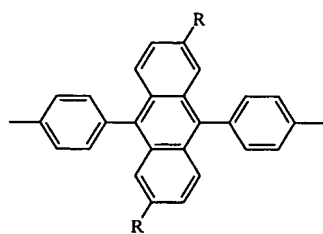
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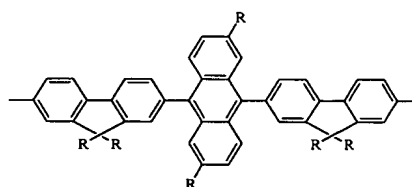
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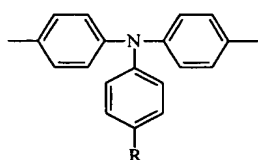
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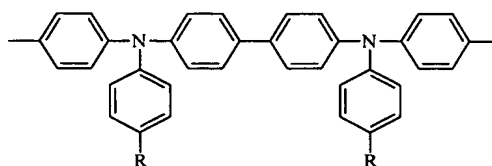
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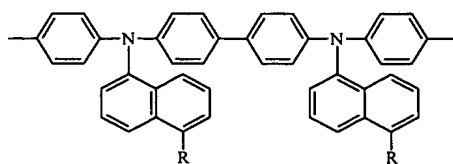
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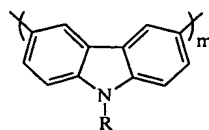
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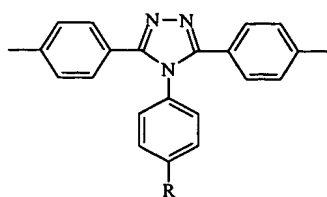
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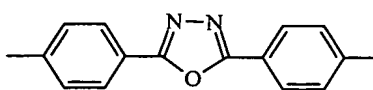
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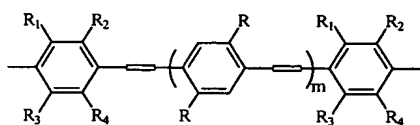
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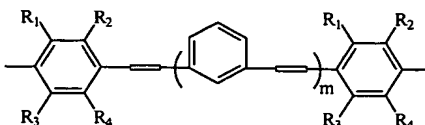
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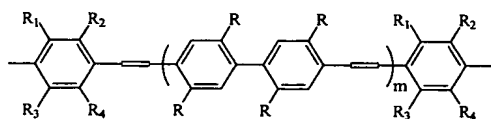
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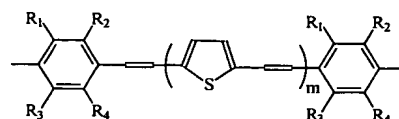
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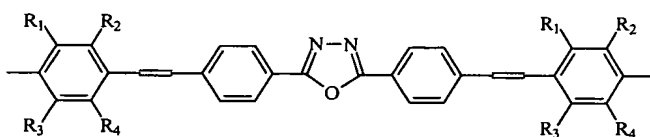
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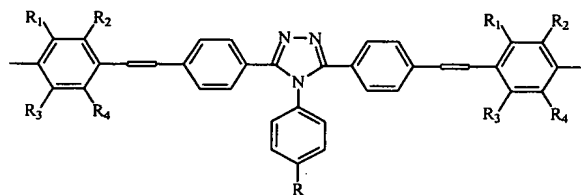
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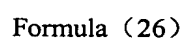
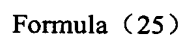
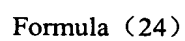
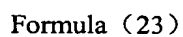
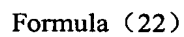
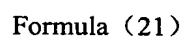
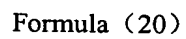
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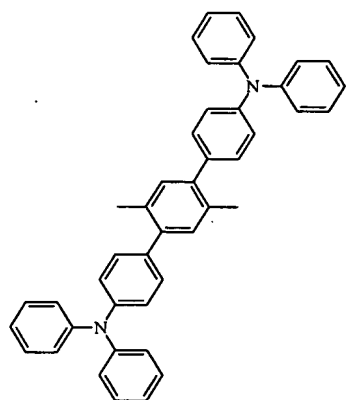


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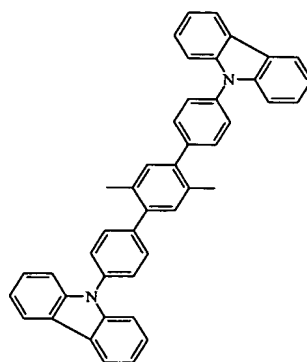


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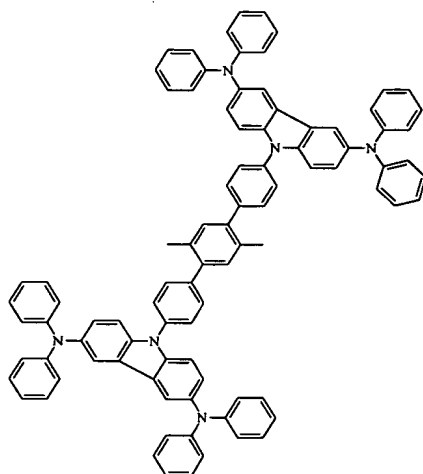




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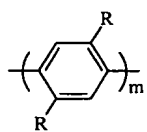
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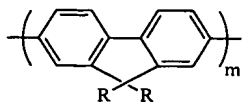
Formula (29)

Ar<sub>2</sub> being one or two luminous structural elements selected from a group consisting of formula (30) – formula (44), wherein R each independently is hydrogen, alkyl, alkoxy, optionally substituted phenyl or naphthyl; m=1-10;

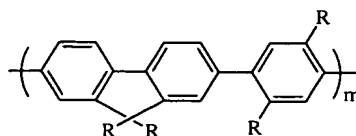




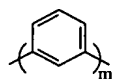
Formula (30)



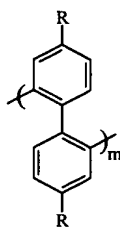
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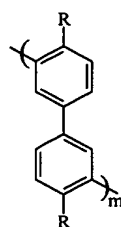
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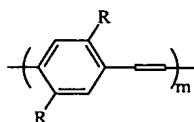
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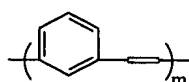
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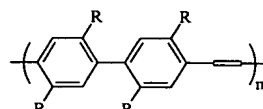
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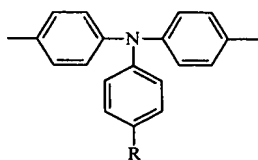
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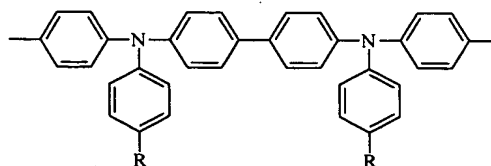
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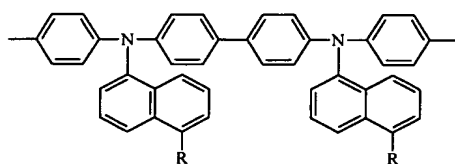
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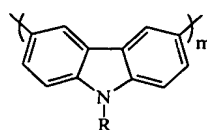
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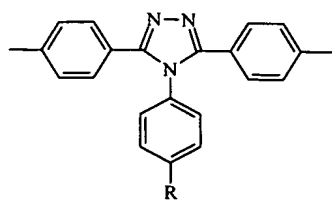
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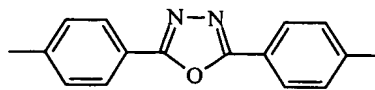
Formula (41)



Formula (42)

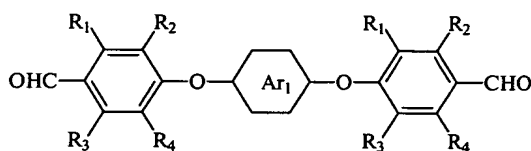


Formula (43)



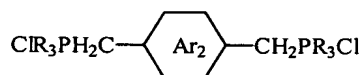
Formula (44)

According to another aspect of the present invention, there is provided a process for preparing said energy-transfer type poly(p-phenylene vinyl) polymeric luminescent material, comprising the step of copolymerizing at least one  $Ar_1$ -containing aromatic dialdehyde monomer represented by general formula (45) and at least one  $Ar_2$ -containing aromatic diphosphonium monomer represented by general formula (46) at an equal molar amount,



Formula (45)

wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  each independently is hydrogen, alkyl, alkoxy, optionally substituted phenyl or naphthyl;  $Ar_1$  is the same as that in above mentioned polymeric structure;



Formula (46)

wherein Ar<sub>2</sub> is the same as that in above-mentioned polymeric structure;  
R is phenyl, ethyl, ethoxyl, propyl, butyl, pentyl, hexyl or octyl.

#### Detailed description of the preferred embodiments

In the present invention, unless otherwise indicated, following terms have the following meanings:

*Alkyl* indicates linear or branched alkyl having 1-18 carbon atoms, optionally substituted with, for example, halogen, amino or nitro.

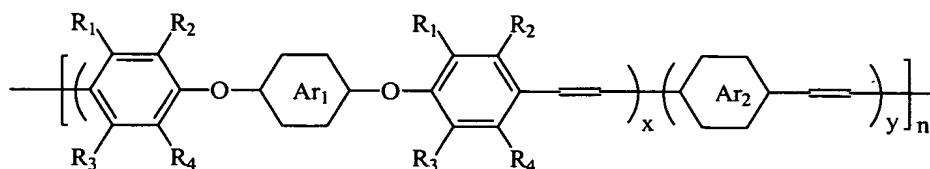
*Alkoxy* indicates the group –OR, wherein R is an alkyl defined as above.

*Halogen* indicates fluorine, chlorine, bromine or iodine.

*Optionally substituted phenyl or naphthyl* indicates optionally substituted phenyl or naphthyl with alkyl, alkoxy, halogenated alkyl, halogen, phenyl, naphthyl, arylamino or diarylamino, or carbozyl, wherein the arylamino or diarylamino includes but are not limited to N,N'-diphenylamino, N-phenyl-N'-1-naphthylamino and N,N'-di(1-naphthylamino).

Next, the technical solution of the present invention will be described in detail.

According to the present invention, there is provided an energy-transfer type poly(p-phenylene vinyl) polymeric luminescent material, which has the structural unit as represented by the following formula (1):

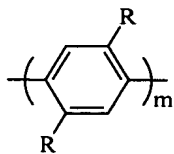


Formula (1)

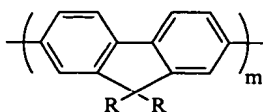
wherein  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  each independently is hydrogen, alkyl, alkoxy, optionally substituted phenyl or naphthyl; preferably,  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  each independently is hydrogen, C1-18 alkyl, C1-18 alkoxy, 4-(N,N'-diphenylamino)phenyl, 4-(N-phenyl-N'-1-naphthylamino)phenyl, 4-[N,N'-di(1-naphthylamino)]phenyl, 4-carbazolylphenyl, phenyl or naphthyl;

$x$  and  $y$  each is the content of the luminous element, satisfying  $0 < x < 1$ ,  $0 < y < 1$ ,  $x + y = 1$ ; and  $n = 1-200$ .

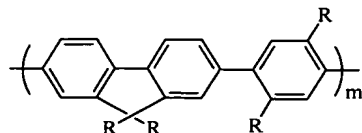
$Ar_1$  being one or two structural luminous elements selected from a group consisting of formula (2) – formula (29), wherein  $R$ ,  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  each independently is hydrogen, alkyl, alkoxy, optionally substituted phenyl or naphthyl; preferably,  $R$ ,  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  each independently is hydrogen, C1-18 alkyl, C1-18 alkoxy, 4-(N,N'-diphenylamino)phenyl, 4-(N-phenyl-N'-1-naphthylamino)phenyl, 4-[N,N'-di(1-naphthylamino)]phenyl, 4-carbazolylphenyl, phenyl or naphthyl; and  $m = 1-10$ ;



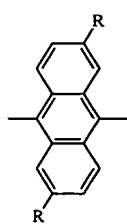
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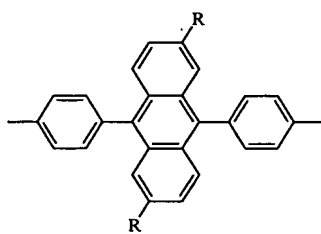
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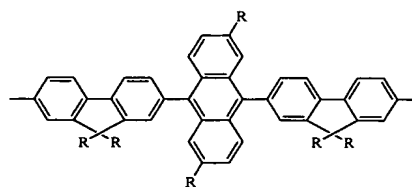
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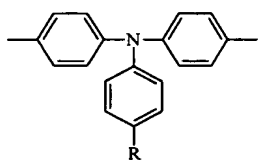
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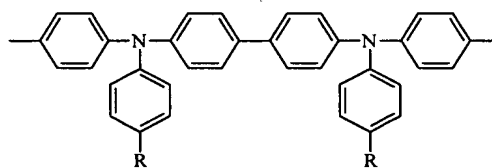
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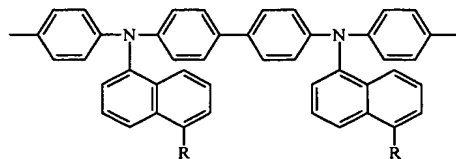
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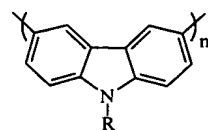
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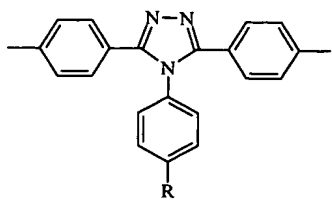
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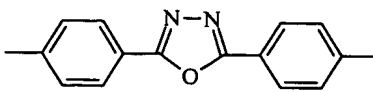
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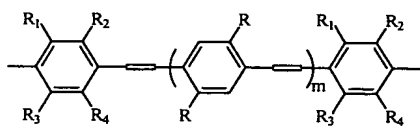
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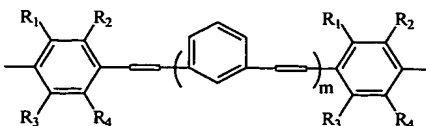
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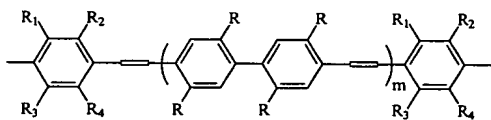
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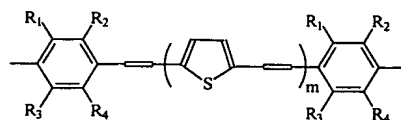
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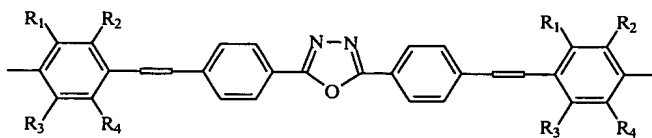
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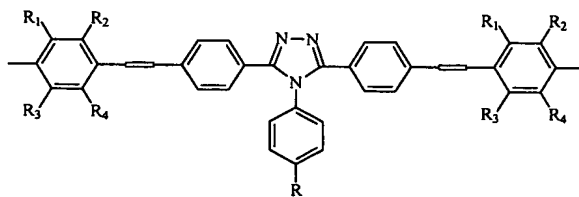
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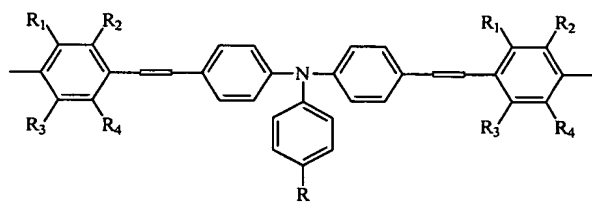
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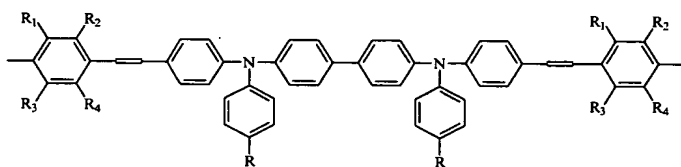
Formula (18)



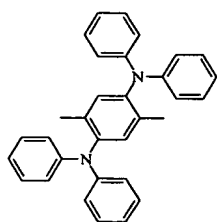
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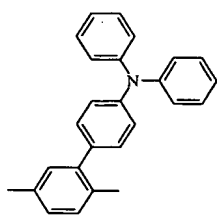
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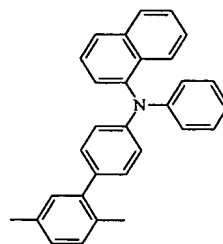
Formula (21)



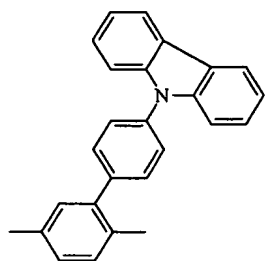
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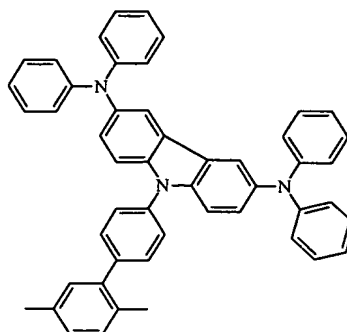
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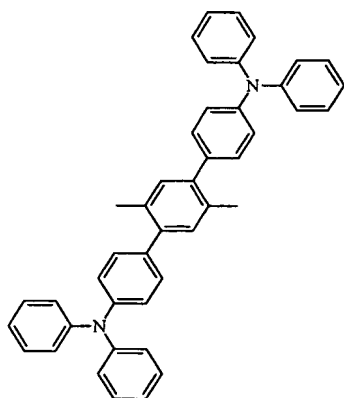
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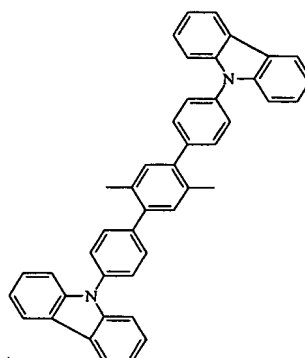
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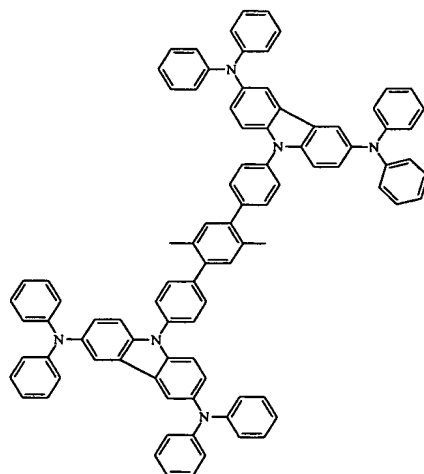
Formula (26)



Formula (27)



Formula (28)

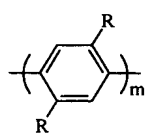


Formula (29)

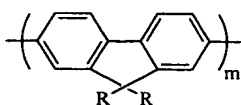
Ar<sub>2</sub> being one or two luminous structural elements selected from a group consisting of formula (30) – formula (44), wherein R each independently



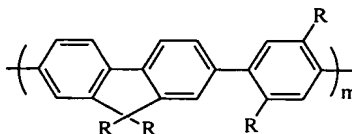
is hydrogen, alkyl, alkoxy, optionally substituted phenyl or naphthyl;  
preferably, R each independently is hydrogen, C1-18 alkyl, C1-18 alkoxy,  
4-(N,N'-diphenylamino)phenyl, 4-(N-phenyl-N'-1-naphthylamino)phenyl,  
4-[N,N'-di(1-naphthylamino)]phenyl, 4-carbazolylphenyl, phenyl or  
naphthyl; and m=1-10;



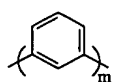
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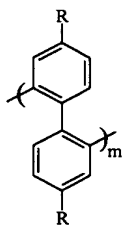
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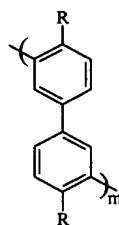
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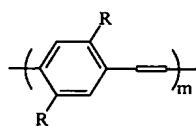
Formula (33)



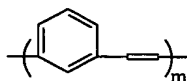
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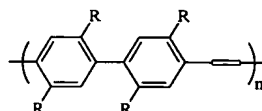
Formula (35)



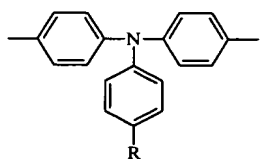
Formula (36)



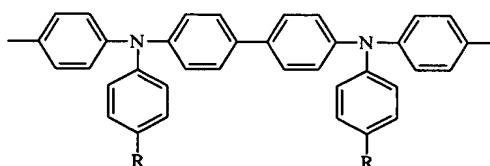
Formula (37)



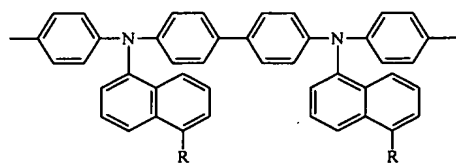
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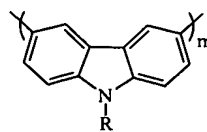
Formula (39)



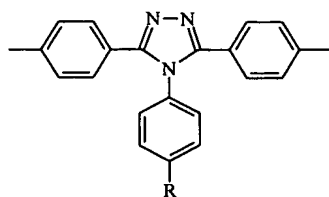
Formula (40)



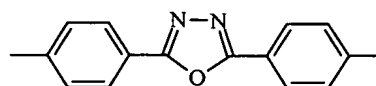
Formula (41)



Formula (42)

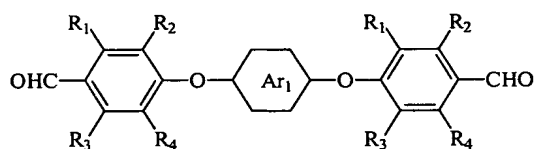


Formula (43)



Formula (44)

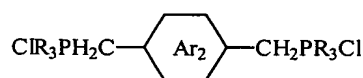
According to the present invention, there is provided a process for preparing said energy-transfer type poly(p-phenylene vinyl) polymeric luminescent material, comprising the step of copolymerizing at least one Ar<sub>1</sub>-containing aromatic dialdehyde monomer represented by general formula (45) and at least one Ar<sub>2</sub>-containing aromatic diphosphenium monomer represented by general formula (46) at an equal molar amount,



Formula (45)

wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> each independently is hydrogen, alkyl, alkoxy, optionally substituted phenyl or naphthyl; preferably R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> each independently is hydrogen, C1-18 alkyl, C1-18 alkoxy, 4-(N,N'-

diphenylamino)phenyl, 4-(N-phenyl-N'-1-naphthylamino)phenyl, 4-[N,N'-di(1-naphthylamino)]phenyl, 4-carbazolylphenyl, phenyl or naphthyl; Ar<sub>1</sub> is defined as in above formula (1);



Formula (46)

wherein Ar<sub>2</sub> is defined as in above formula (1); R is phenyl, ethyl, ethoxyl, propyl, butyl, pentyl, hexyl or octyl.

The aromatic dialdehyde monomer containing an ether bond as represented by formula (45) can be prepared by the following method.

4,4'-dihydroxy substituted Ar<sub>1</sub> and p-fluorobenzaldehyde at a molar ratio of 1:2-3 are dissolved in N,N'-dimethylformamide to produce a solution. The solution is refluxed in the presence of anhydrous K<sub>2</sub>CO<sub>3</sub> at a molar ratio of 1:2 for 2-24 hrs. The solution is cooled. Then the product is precipitated with anhydrous ethanol, filtered and washed with water, dried, and finally separated by column chromatography to obtain an aromatic Ar<sub>1</sub> dialdehyde monomer containing an ether bond (purity above 99%).

The aromatic diphosphonium monomer represented by formula (46) can be prepared by the following method.

An aromatic Ar<sub>2</sub> di(benzylchloride) and triphenylphosphine or tributylphosphine at a molar ratio of 1: 2-3 are dissolved in N,N'-

dimethylformamide to form a mixture. The mixture is reacted for 1-24 hrs at 120°C under  $N_2$  atmosphere. Then the reaction mixture is cooled to room temperature. The product is precipitated with a great quantity of diethyl ether, then washed with diethyl ether for several times, filtered and dried to obtain an aromatic  $Ar_2$  diphosphonium monomer.

In a specific embodiment according to the present invention, the poly(p-phenylene vinyl) polymeric luminescent material in which two different luminous elements coexist can be prepared by the following method:

a poly(p-phenylene vinyl) polymeric luminescent material, in which different luminous elements are fully isolated by an ether bond, is prepared through Wittig reaction, comprising:

The aromatic  $Ar_1$  dialdehyde monomer and the aromatic  $Ar_2$  diphosphonium monomer at an equal molar amount are dissolved in anhydrous trichloromethane. Then a solution of sodium ethanolate in ethanol at a molar ratio of 1:2-6 is added. The resultant mixture is reacted for 1-12 hrs with magnetic stirring under  $N_2$  atmosphere. The reaction is stopped by the addition of 0.1N hydrochloric acid. The resultant mixture is extraction-separated with dichloromethane. The organic phase is collected and washed 3 times with 0.1N dilute hydrochloric acid, 3 times with 0.1N ammonia solution, and finally washed several times with water. The washed organic phase is dried with anhydrous  $Na_2SO_4$ , and

concentrated in a rotary evaporator. The product is settled in methanol to obtain the crude product of a polymeric luminescent material. The crude product is extracted with acetone, dissolved and settled 3 times respectively with chloroform and methanol, and vacuum dried to obtain a purified polymeric luminescent material.

In another specific embodiment according to the present invention, a poly(p-phenylene vinylene) polymeric luminescent material, in which more than two kinds of different luminous elements co-exist, can be prepared as follows:

The process for preparing a poly(p-phenylene vinylene) polymeric luminescent material in which two or more luminous elements coexist is substantially the same as above, except that there are two or more aromatic  $Ar_1$  dialdehyde monomers and two or more aromatic  $Ar_2$  diphosphonium monomers, satisfying that the total moles of aromatic  $Ar_1$  dialdehyde monomers is equal to that of aromatic  $Ar_2$  diphosphonium monomers.

Though not bound to any theory, it is believed that, according to the present invention, a conjugated polymeric oligomer capable of emitting long wave and a conjugated polymeric oligomer capable of emitting short wave are alternatively and randomly copolymerized to the backbone of a polymer through Wittig reaction to form an energy transfer type poly(p-phenylene vinyl) polymeric luminous material having two or more kinds

of luminous elements in the backbone. The conjugated length of each kind of luminous element can be adjusted and different luminous elements can be effectively isolated by an ether bond as a linking element and a isolating element. Meanwhile, different luminous elements can independently radiate, which provides the precondition of energy transfer between different luminous elements in relation to molecular structure and therefore the fluorescence quantum efficiency can be improved.

The following examples are just to explain the present invention and in no way limit the present invention.

Example 1: Synthesis of 1, 4-dichloromethyl phenyl di(tributyl phosphinium )

17.5g (100 mmol) of 1,4-dibenzylchloride and 60.6g (300 mol) of tributylphosphine were dissolved in 30 ml of N,N-dimethylformamide to form a solution. The solution was refluxed at 120°C for 12 hrs under N<sub>2</sub> atmosphere. Then the solution was cooled, poured into a great quantity of diethyl ether. The solution was washed repeatedly with diethyl ether, filtered and dried to obtain a white solid, yield~90%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz, ppm): 7.62 (s, 4H), 4.42 (d, J = 14.8 Hz, 4H), 2.38 (t, 12H), 1.49 (m, 24H), 0.93 (t, 18H).

FT-IR (KBr): 2960, 2932, 2873, 2797, 1514, 1464, 1100, 860 cm<sup>-1</sup>.

Example 2: Synthesis of 1,3-dichloromethylphenyl di(tributyl phosphinium )

The procedures were the same as those in example 1, except that 17.5 g (100 mmol) of 1,3-dibenzylchloride was used in place of 1,4-dibenzylchloride. The yield~90%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz, ppm): 8.21 (s, 1H), 7.56 (d, 2H), 7.40 (t, 1H), 4.33 (d, J = 15.6 Hz, 4H), 2.40 (m, 12H), 1.49 (m, 24H), 0.95 (t, 18H).

Example 3: Synthesis of 2,5-dichloromethylthienyl di(tributyl phosphinium )

18.0g (100 mmol) of 2,5-dichloromethylthiophene and 60.6g (300 mol) of tributylphosphine were dissolved in 30 ml of N,N-dimethylformamide to form a solution. The solution was refluxed at 120 °C for 12 hrs under N<sub>2</sub> atmosphere. The solution was cooled, poured into a great quantity of diethyl ether. The solution was washed repeatedly with diethyl ether, filtered and dried to obtain a light yellow solid, yield~85%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz, ppm): 7.23 (s, 2H), 4.68 (d, J = 12.8 Hz, 4H), 2.43 (m, 12H), 1.49 (m, 24H), 0.95 (t, 18H).

Example 4: Synthesis of 4,4'-dichloromethylbiphenyl di(tributyl phosphinium )

The procedures were the same as those in example 1, except that 25.1 g (100 mol) of 4,4'-dichloromethylbiphenyl was used in place of 1,4-dibenzylchloride to obtain a white solid. The yield~90%.

Example 5: Synthesis of 2,5-di(4-tributylphosphinochloromethylphenyl)-1,3,4-oxadiazole

The procedures were the same as those in example 1, except that 31.9 g (100 mmol) of 2,5-di(4-chloromethylphenyl)-1,3,4-oxadiazole was used in place of 1,4-dibenzylchloride to obtain a light yellow solid. The yield~80%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, δppm); 8.0 (d, 4H), 7.6 (d, 4H), 4.8 (d, 4H), 2.4 (m, 12H), 1.5 (m, 24H), 0.9 (t, 18H).

Example 6: Synthesis of 4-phenyl-3, 5-di(4-tributylphosphinochloromethylphenyl)-1,2,4-triazole

The procedures were the same as those in example 1, except that 39 g (100 mmol) of 4-phenyl-3, 5-di(4-tributylphosphinochloromethylphenyl)-1,2,4-triazole was used in place of 1,4-dibenzylchloride to obtain a light green solid. The yield~73%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, δppm); 7.5-7.8 (m, 13H), (d, 4H), 4.8 (d, 4H), 2.4 (m, 12H), 1.5 (m, 24H), 0.9 (t, 18H).



Example 7 Synthesis of 2-methoxyl-5-(2'-ethylhexyoxyl)-1,4-di(2'-((3',5'-dimethoxyl)-4'-hydroxylphenyl)vinyl) benzene

4.8g of NaH (60%, 200mmol) was dissolved in 50ml of an anhydrous DMF under nitrogen atmosphere to form a mixture. Then 50ml of a solution of 13.0g (20mmol) of 2-methoxyl-5-(2'-ethylhexyoxyl)-1,4-di(butyloxyphosphate) xylene in DMF was slowly added drop-wise into the mixture with magnetic stirring. The resultant mixture was reacted at room temperature for six hours. Then a solution of 7.5g (41mmol) of 3,5-dimethoxylp-hydroxylbenzaldehyde in DMF was slowly added dropwise into the mixture. The resultant mixture was reacted at room temperature under nitrogen atmosphere for about another 12 hours. Finally the reaction was stopped by adding 100ml of 1N dilute hydrochloric acid. The yellow precipitate formed was filtered, extracted, dried and separated by column chromatogram (The eluate is ethyl acetate : petroleum ether=1:1(V/V)) to obtain a bright yellow solid 9.7g. The yield was 83%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, δppm); 7.0-7.4 (m, 10H), 5.6 (s, 2H), 3.9 (m, 17H), 0.9-1.8 (m, 17H).

Example 8 Synthesis of 2-methoxyl-5-(2'-ethylhexyloxy)-1,4-di(2'-(4'-hydroxylphenyl)vinyl) benzene

The procedures were the same as those in example 7, except that 5.0g

(41mmol) of p-hydroxylbenzaldehyde was used in place of 3,5-dimethoxyl p-hydroxylbenzaldehyde, to obtain a yellow solid. The yield was 80%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, δppm); 7.0-7.4 (m, 10H), 5.6 (s, 2H), 3.9 (m, 5H), 0.9-1.8 (m, 17H).

Example 9 Synthesis of 1,4-di(2'-((3',5'-dimethoxyl)-4'-hydroxylphenyl)vinyl)benzene

40ml of a solution of 9.8g (20mmol) of 1,4-di(butyloxyphosphate) xylene in DMF was added drop-wise into a 50ml DMF solution containing 4.8g (200mmol) NaH (60%) under nitrogen atmosphere. The resultant mixture was reacted at room temperature for 24hrs with magnetic stirring. Then 50ml of a solution of 7.5g (41mmol) of 3,5-dimethoxyl-p-hydroxylbenzaldehyde in DMF was added. The reaction continued for another 12hrs. The reaction was stopped by adding dilute hydrochloric acid. The reaction product was filtered, dried and separated by column chromatogram to obtain a bright yellow solid emitting strong fluorescence 8.5g. The yield was 82%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, δppm): 6.8-7.4 (m, 10H), 4.7 (s, 2H), 4.0 (m, 12H).

Example 10 Synthesis of 2,5-dihexyloxyl-1,4-di(2'-((3',5'-dimethyloxyl)-4'-hydroxyphenyl)vinyl) benzene

The procedures were the same as those in example 7, except that 13.8g (20mmol) of 2,5-dihexyloxyl-1,4-di(butyloxylphosphate) xylene was used in place of 2-methoxyl-5-(2'-ethylhexyloxyl)-1,4-di(butyloxylphosphate) xylene, to obtain a light yellow solid 11.8g. The yield was 80%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, δppm): 6.8-7.4 (m, 12H), 5.5 (s, 2H), 3.9-4.1 (m, 16H), 0.9-1.8(m, 22).

Example 11 Synthesis of 1,4-di(2'-((3',5'-dimethoxy-4'-(4'-formaldehydephenyloxyl)phenyl)vinyl) benzene

4.3g (10mmol) of 1,4-di(2'-((3',5'-dimethoxy-4'-hydroxyphenyl)vinyl) benzene, 5.0g (40mmol) of p-fluorobenzaldehyde and 2.7g (20mmol) of anhydrous potassium carbonate were dissolved in 50ml of N,N-dimethylformamide to produce a mixture. The mixture was refluxed 24hrs under nitrogen atmosphere. The reaction product was precipitated with methanol, filtered and washed with distilled water, and then dried and separated by column chromatogram (eluate is dichloromethane) to obtain a yellow solid 5.0g. The yield was 80%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, δppm); 10.2 (s, 2H), 7.0-7.4 (m, 20H), 3.9 (t, 12H).

Example 12 Synthesis of 3-methoxyl-5-(2-ethylhexyloxy)-1,4-di(2'-(3',5'-dimethoxyl-4'-(4'-formaldehydephenyloxy)phenyl)vinyl) benzene  
6.0g (10mmol) of 3-methoxyl-5-(2-ethylhexyloxy)-1,4-di(2'-(3',5'-dimethoxyl-4'-hydroxylphenyl)vinyl)benzene, 5.0g (40mmol) of p-fluorobenzaldehyde and 2.7g (20mmol) of anhydrous potassium carbonate were dissolved in 50ml of N,N-dimethylformamide to produce a mixture. The mixture was refluxed 24hrs under nitrogen atmosphere. The reaction product was precipitated with methanol, filtered and washed with distilled water, and then dried and separated by column chromatogram to obtain a yellow solid 6.4g. The yield was 82%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, δppm); 10.2 (s, 2H), 7.0-7.4 (m, 18H), 3.9 (m, 17H), 0.9-1.8 (m, 17H).

Example 13 Synthesis and characterization of a polymeric luminous material P1

0.29g (0.5mmol) of 1,4-dichloromethylphenyl tributylphosphine salt and 0.40g (0.5mmol) of 2-methoxyl-5-(2-ethylhexyloxy)-1,4-di(2'-(3',5'-dimethoxyl-4'-(4'-formaldehydephenyloxy)phenyl)vinyl) benzene were dissolved in 10ml of anhydrous trichloromethane to form a mixture. Then 3ml of a 0.3N solution of sodium ethanolate in ethanol was added drop-wise. The resultant mixture was reacted for 5 hrs under nitrogen atmosphere. The reaction was stopped by the addition of dilute

hydrochloric acid. The reaction product was extracted with dichloromethane, washed 3 times with 0.1N dilute hydrochloric acid, washed 3 times with 0.1N ammonia, and washed with water for several times. The product was dried, concentrated, precipitated with methanol, thermally-extracted with acetone and vacuum dried to obtain a yellow fibrous product P1. The yield was 70%.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz, ppm): 7.53~6.86, 3.97~3.84, 1.56~0.88. Elemental calcd for  $(\text{C}_{35}\text{H}_{42}\text{O}_7)(\text{C}_{22}\text{H}_{16}\text{O})$ : C, 78.62; H, 6.67. Found: C, 78.12; H, 6.73.

The final product had a weight average molecular weight of  $3.8 \times 10^4$ , a number average molecular weight of  $2.0 \times 10^4$ , and a maximal luminous peak at 500nm in the fluorescence spectrum in the form of a thin film.

A single-layer element having a structure ITO/PEDOT/P1/Ca/Al was assembled as follows. A pre-cleaned ITO glass was used as an anode. A layer of conductive polymer, a derivative of polythiophene (PEDOT) was spin coated on the surface of the anode and the thickness of the layer was 100nm. The PEDOT-coated ITO was vacuum dried for one hour at  $100^\circ\text{C}$ . Then a 10mg/ml solution of P1 in chloroform was spin coated on the surface of the ITO at 1500rpm. Next, calcium metal and aluminum metal were deposited at a high vacuum, respectively having a thickness of 10nm and 100nm. The obtained single-layer element had the

performances of a turn-on voltage of 8.8V, the maximal luminance of 190cd/m<sup>2</sup>, a maximal luminous efficiency of 0.042cd/A and a maximal electroluminescence peak at 505nm.

#### Example 14 Synthesis and characterization of a polymeric luminous material P2

The procedures were the same as those in example 13, except that 1.36g (1.88mmol) of 2,5-di(4-tributylphosphinochloromethylphenyl)-1,3,4-oxadiazole and 1.50g (1.88mmol) of 3-methoxyl-5-(2-ethylhexyloxyl)-1,4-di(2'-(3',5'-dimethoxyl-4'-(4'-formaldehydephenyloxyl)phenyl)vinyl) benzene were dissolved in 50ml of chloroform to form a mixture. A yellow fibrous solid P2 was obtained and the yield was 60%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, ppm): 8.10, 7.53~6.86, 3.97~3.84, 1.56~0.88.

Elemental calcd for (C<sub>35</sub>H<sub>42</sub>O<sub>7</sub>)(C<sub>22</sub>H<sub>16</sub>O)<sub>0.8</sub>(C<sub>30</sub>H<sub>20</sub>O<sub>2</sub>N<sub>2</sub>)<sub>0.2</sub>: C, 78.22: H, 6.54: N, 0.62 Found: C, 78.30: H, 6.42: N, 0.55.

The final product had a weight average molecular weight of 4.0 X 10<sup>4</sup>, a number average molecular weight of 2.0 X 10<sup>4</sup>, and a maximal luminous peak at 500nm in the fluorescence spectrum in the form of a thin film.

A single-layer element was assembled as in example 13. The obtained single-layer element had the performances of a turn-on voltage

of 7.0V, a maximal luminance of 450cd/m<sup>2</sup>, a maximal luminous efficiency of 0.07cd/A and a maximal electroluminescence peak at 501nm.

#### Example 15 Synthesis and characterization of a polymeric luminous material P3

The procedures were the same as those in example 13, except that 0.68g (0.935mmol) of 2,5-di(4-tributylphosphinochloromethylphenyl)-1,3,4-oxadiazole, 1.50g (1.87mmol) of 3-methoxyl-5-(2-ethylhexyloxy)-1,4-di(2'-(3',5'-dimethoxyl-4'-(4'-formaldehydephenyloxy)phenyl)vinyl)benzene and 0.5g (0.935mmol) of 1,4-dichloromethylphenyltributylphosphino salt were dissolved in 50ml of chloroform to form a mixture. A yellow fibrous solid P3 was obtained and the yield was 70%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, ppm): 8.10, 7.63~6.86, 3.97~3.84, 1.56~0.88(m, 15H).

Elemental calcd for (C<sub>35</sub>H<sub>42</sub>O<sub>7</sub>)(C<sub>22</sub>H<sub>16</sub>O)<sub>0.5</sub>(C<sub>30</sub>H<sub>20</sub>O<sub>2</sub>N<sub>2</sub>)<sub>0.5</sub>: C, 77.71: H, 6.37: N, 1.49. Found: C, 78.30: H, 6.42: N, 1.57.

The final product had a weight average molecular weight of 3.5 X 10<sup>4</sup>, a number average molecular weight of 2.9 X 10<sup>4</sup>, and a maximal luminous peak at 500nm in the fluorescence spectrum in the form of a thin film.

A single-layer element was assembled as in example 13. The

obtained single-layer element had the performances of a turn-on voltage of 7.3V, the maximal luminance of 625cd/m<sup>2</sup>, maximal luminous efficiency of 0.18cd/A and maximal electroluminescence peak at 501nm.

#### Example 16 Synthesis and characterization of a polymeric luminous material P4

The procedures were the same as those in example 13, except that 0.72g (1mmol) of 2,5-di(4-tributylphosphinochloromethylphenyl)-1,3,4-oxadiazole and 0.80g (1mmol) of 3-methoxyl-5-(2-ethylhexyloxy)-1,4-di(2'-(3',5'-dimethoxyl-4'-(4'-formaldehydephenyloxy)phenyl)vinyl)benzene were dissolved in 50ml of chloroform to form a mixture and 1.5ml of a 0.5N solution of sodium ethanolate in ethanol was added dropwise. A light yellow fibrous solid P4 was obtained and the yield was about 73%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, ppm): 8.14, 7.63~6.86, 3.97~3.84, 1.56~0.88.

Elemental calcd for (C<sub>35</sub>H<sub>42</sub>O<sub>7</sub>) (C<sub>30</sub>H<sub>20</sub>O<sub>2</sub>N<sub>2</sub>): C, 76.92; H, 6.11; N, 2.76. Found: C, 77.10; H, 6.0; N, 2.82.

The final product had a weight average molecular weight of 3.1 X 10<sup>4</sup>, a number average molecular weight of 2.3 X 10<sup>4</sup>, and a maximal luminous peak at 500nm in the fluorescence spectrum in the form of a thin film.

A single-layer element was assembled as in example 13. The



obtained single-layer element had the performances of a turn-on voltage of 7V, the maximal luminance of 1250cd/m<sup>2</sup>, and a maximal luminous efficiency of 0.30cd/A.

#### Example 17 Synthesis and characterization of a polymeric luminous material P5

The procedures were the same as those in example 13, except that 0.20g (0.25mmol) of 4-phenyl-3,5-di(4-tributylphosphinochloromethylphenyl)-1,2,4-triazole, 0.58g (1.0mmol) of 1,4-dichloromethylphenyltributylphosphino salt and 1.0g (1.25mmol) of 3-methoxyl-5-(2-ethylhexyloxy)-1,4-di(2'-(3',5'-dimethoxyl-4'-(4'-formaldehydephenyloxy)phenyl)vinyl) benzene were dissolved in 50ml of chloroform to form a mixture. A yellow fibrous solid P5 was obtained and the yield was 74%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, ppm): 7.53~6.86, 3.97~3.84, 1.56~0.88.

Elemental calcd for (C<sub>35</sub>H<sub>42</sub>O<sub>7</sub>)(C<sub>22</sub>H<sub>16</sub>O)<sub>0.8</sub>(C<sub>36</sub>H<sub>25</sub>O<sub>2</sub>N<sub>3</sub>)<sub>0.2</sub>: C, 78.53: H, 6.54: N, 0.92. Found: C, 78.68: H, 6.42: N, 1.03.

The final product had a weight average molecular weight of 2.6 X 10<sup>4</sup>, a number average molecular weight of 1.5 X 10<sup>4</sup>, and a maximal luminous peak at 500nm in the fluorescence spectrum in the form of a thin film.

A single-layer element was assembled as in example 13. The

obtained single-layer element had the performances of a turn-on voltage of 7.8V, maximal luminance of 131cd/m<sup>2</sup>, a maximal luminous efficiency of 0.089cd/A and a maximal electroluminescence peak at 502nm.

#### Example 18 Synthesis and characterization of a polymeric luminous material P6

The procedures were the same as those in example 13, except that 0.50g (0.63mmol) of 4-phenyl-3,5-di(4-tributylphosphinochloromethylphenyl)-1,2,4-triazole, 0.36g (0.63mmol) of 1,4-dichloromethylphenyltributylphosphine salt and 1.0g (1.25mmol) of 3-methoxyl-5-(2-ethylhexyloxy)-1,4-di(2'-(3',5'-dimethoxyl-4'-(4'-formaldehydephenyloxy)phenyl)vinyl) benzene were dissolved in 50ml of chloroform to form a mixture. A yellow fibrous solid P6 was obtained and the yield was 82%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, ppm): 7.53~6.86, 3.97~3.84, 1.56~0.88.

Elemental calcd for (C<sub>35</sub>H<sub>42</sub>O<sub>7</sub>)(C<sub>22</sub>H<sub>16</sub>O)<sub>0.5</sub>(C<sub>36</sub>H<sub>25</sub>O<sub>2</sub>N<sub>3</sub>)<sub>0.5</sub>: C, 78.41: H, 6.38: N, 2.14. Found: C, 79.32: H, 6.08: N, 2.27.

The final product had a weight average molecular weight of 2.2 X 10<sup>4</sup>, a number average molecular weight of 1.3 X 10<sup>4</sup>, and a maximal luminous peak at 500nm in the fluorescence spectrum in the form of a thin film.

A single-layer element was assembled as in example 13. The

obtained single-layer element had the performances of a turn-on voltage of 7.3V, the maximal luminance of 338cd/m<sup>2</sup>, a maximal luminous efficiency of 0.20cd/A and a maximal electroluminescence peak at 503nm.

#### Example 19 Synthesis and characterization of a polymeric luminous material P7

The procedures were the same as those in example 13, except that 0.50g (0.63mmol) of 4-phenyl-3,5-di(4-tributylphosphinochloromethylphenyl)-1,2,4-triazole and 0.50g (0.63mmol) of 3-methoxyl-5-(2-ethylhexyloxyl)-1,4-di(2'-(3',5'-dimethoxyl-4'-(4'-formaldehydephenyloxyl)phenyl)vinyl) benzene were dissolved in 50ml of chloroform to form a mixture. A yellow fibrous solid P7 was obtained and the yield was 77%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, ppm): 7.53~6.86, 3.97~3.84, 1.56~0.88. Elemental calcd for (C<sub>35</sub>H<sub>42</sub>O<sub>7</sub>) (C<sub>36</sub>H<sub>25</sub>O<sub>2</sub>N<sub>3</sub>): C, 78.24; H, 6.15; N, 3.86. Found: C, 80.02; H, 5.94; N, 3.83.

The final product had a weight average molecular weight of 2.5 X 10<sup>4</sup>, a number average molecular weight of 1.4 X 10<sup>4</sup>, and a maximal luminous peak at 500nm in the fluorescence spectrum in the form of a thin film.

A single-layer element was assembled as in example 13. The

obtained single-layer element had the performances of a turn-on voltage of 6.3V, the maximal luminance of 256cd/m<sup>2</sup>, a maximal luminous efficiency of 0.19cd/A and a maximal electroluminescence peak at 501nm.

#### Example 20 Synthesis and characterization of a polymeric luminous material P8

The procedures were the same as those in example 13, except that 0.29g (0.5mmol) of 1,3-dichloromethylphenyltributyl phosphine was used in place of 1,4-dichloromethylphenyltributyl phosphine. A yellow fibrous solid P8 was obtained and the yield was 81%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz, ppm): 7.50~6.84 (m, 24H), 3.99~3.82 (m, 17H), 1.56~0.88(m, 15H).

Elemental calculated for (C<sub>35</sub>H<sub>42</sub>O<sub>7</sub>)(C<sub>22</sub>H<sub>16</sub>O): C, 78.62; H, 6.67; Found: C, 78.32; H, 6.71.

The final product had a weight average molecular weight of 5.2 X 10<sup>4</sup>, a number average molecular weight of 2.3 X 10<sup>4</sup>, and a maximal luminous peak at 500nm in the fluorescence spectrum in the form of a thin film.

A single-layer element was assembled as in example 13. The obtained single-layer element had the performances of a turn-on voltage of 8.8V, the maximal luminance of 800cd/m<sup>2</sup>, a maximal luminous